Art. XIV.—*The Occurrence of Helium in a Spa Gas from Daylesford, Victoria.*

By G. A. AMPT and E. J. HARTUNG.

Shortly after the discovery of helium in the mineral cleveite by Professor Ramsay in 1895. numerous terrestrial sources of the new element were found. The gases arising from mineral springs proved to contain helium in small amount, and later it was also discovered in the natural gases associated with petroleum wells in America. Some of these gases were shown to contain more than 1% of helium by volume, and large quantities of the element are now extracted commercially by processes of liquefaction and fractional distillation. The largest amount of helium yet found in any natural gas, 5·4% by volume, occurs in a spa gas from Mazières, France. Many of these helium-containing gases are distinctly radioactive.

As far as we are aware, the presence of helium has not hitherto been recorded in any natural gas from Australian sources. A few years ago, one of the Daylesford spa gases was suspected to be radioactive as the result of some experiments carried out by Mr. James Macdonald, manager of Hepburn Spa, Ltd. This suspected activity was confirmed by Sir David Masson and one of us (G.A.) in 1919, and the radioactive material was proved to be radium emanation (radon), present in extremely small amount. Traces of helium must therefore inevitably have been present in this spa gas as one of the products of radioactive change. We have recently carried out a chemical investigation of gas from the same source with the object of finding out whether helium was present in more than minute amount. The general procedure in such cases is to treat the gas with an alkaline liquid to absorb carbon dioxide and other acidic gases, to remove oxygen by absorption in suitable reagents, and to burn hydrogen and other combustible gases by sparking with pure oxygen. The nitrogen is then absorbed by treatment with hot magnesium or calcium, and the residue consists of inert gases of the argon group. Separation of this residue into its constituents involves tedious fractional distillations and adsorptions by cooled charcoal. If only two members of the inert group can be shown to be present, a simple density determination of the gas enables their relative amounts to be calculated without any separation being attempted.

Our analysis of the gas was based on these general lines and consequently involves nothing essentially new. Nevertheless, we feel that the detection of helium in an Australian natural gas for the first time is of sufficient interest to be recorded here.

Two separate samples of the spa gas were examined; they were received in metal cylinders under pressure. and had been drawn

direct from the gasometer built over the mineral spring at Daylesford. On arrival in Melbourne, the gas was found to be distinctly radioactive. Preliminary tests showed that gases other than carbon dioxide were present to the extent of only 3 per cent. approximately, and subsequently it was found that the two samples were very similar in composition except, however, that one appeared to have been contaminated slightly with air during collection.

The procedure in each case was the same. Several accurate analyses on small samples were made to determine the carbon dioxide content, and then large volumes of the gas (over 100 litres) were treated with sodium hydroxide solution to free them completely from this constituent. Samples of the remainder were analyzed accurately for oxygen by treatment with alkaline pyrogallate solution and, after complete removal of this element, the residue was examined for hydrogen and other combustible gases, which were proved to be absent. The volume of the gas was now
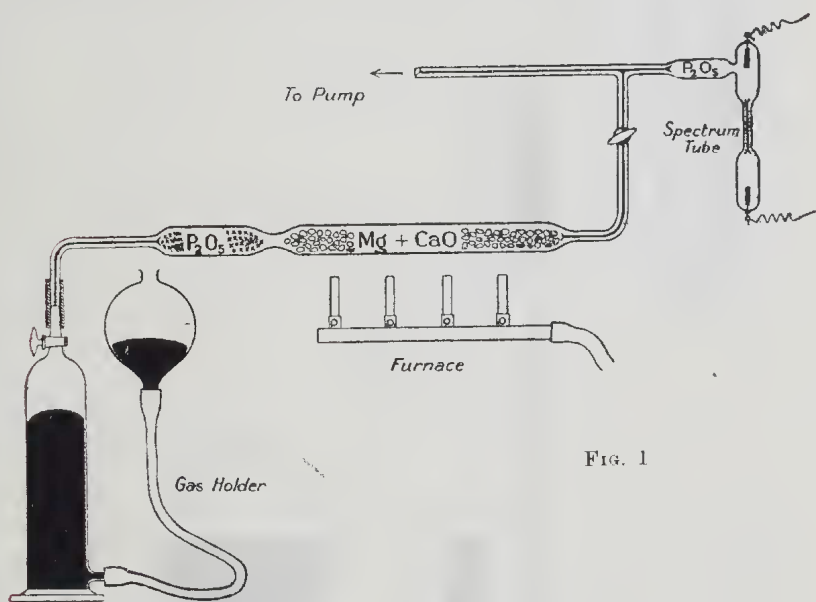

Fig. 1

about $2\frac{1}{2}$ litres and consisted of nitrogen and gases of the argon group. The bulk of the nitrogen was removed by slow passage over red-hot magnesium turnings contained in an iron tube about a metre long.

This treatment reduced the volume of the gas to about 200 c.c., but contaminated it with hydrogen due to the action of traces of water vapour on the magnesium. Complete removal of the remaining nitrogen was effected by passing the gas through a heated layer of an intimate mixture of calcium oxide and magnesium powder contained in a hard glass tube (Fig. 1).

The mixture must be carefully made from recently ignited quicklime, which is quite free from hydroxide and carbonate, otherwise dangerous explosions may result when it is heated.

It was found to be extremely efficient as a nitrogen absorbent, but gave off hydrogen continuously on heating in spite of the greatest care in excluding water vapour. This hydrogen was
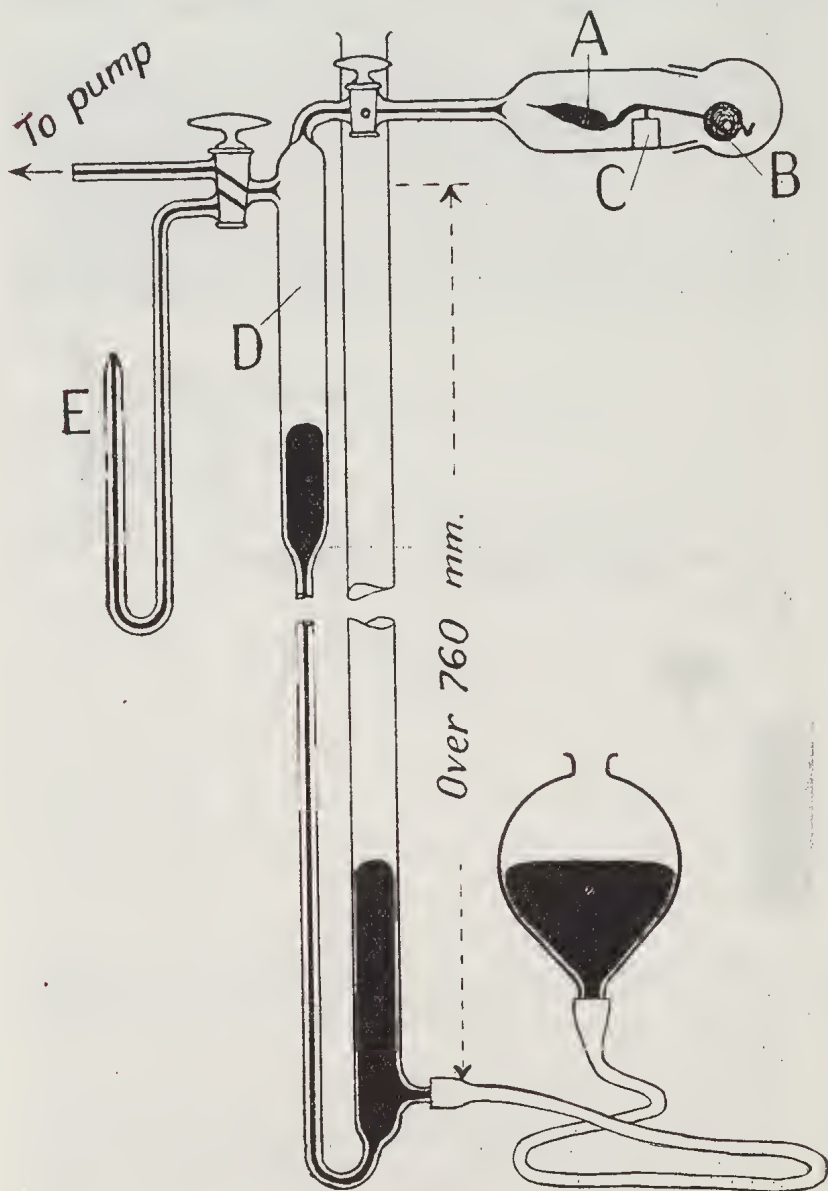

Fig. 2

removed from the residual gas by sparking with pure oxygen and, finally, the volume of the argon group gases was measured.

The volume compositions of the two samples of spa gas were found to be:—

		I.	II.
		%	%
Carbon dioxide	-	97·30	96·95
Nitrogen	-	2·30	2·55
Oxygen	-	0·37	0·46
Inert gases	-	0·034	0·045

The differences between the two samples may be accounted for by slight contamination of II. with air.

The total volume of inert gases at our disposal was now 47·8 c.c., measured at N.T.P.

Its spectrum was carefully mapped, more than 70 lines being measured. Many of these were faint, and could not be identified, but 23 coincided with known argon lines. Three of the most prominent helium lines were found, one ($\lambda = 6678$) being bright, and the others (5876 and 5016) fainter. Some very faint lines occurred in the positions of brilliant lines in the spectrum of pure neon. The gas was re-purified from possible traces of nitrogen without alteration to its volume or its spectrum. It appeared, therefore, to consist of argon with some helium and a small quantity of neon.

The separation of the gases of the argon group from one another involves much tedious work, and we did not consider the attempt in this case worth while. However, the density was determined as a guide to the approximate composition of the sample. This was performed by means of an Aston silica density balance. This instrument was developed by Aston in 1914 (*Proc. Roy. Soc.* 89A, 439) on the principle of the now well-known Steele-Grant microbalance. A very light silica beam A (Fig. 2) oscillates about a single central knife edge, and carries at one end a sealed silica bulb B containing air.

A pointer at the other end is observed by a microscope, and serves to determine the position of the beam. The balance rests on a polished, horizontal quartz plate C cemented inside a small glass tube, and is kept central by a light ring of silica through which the pointer passes. The case of the instrument communicates by a capillary tube with a manometer D, which is in connection with a small Toepler pump and also with a gas syphon tube E, which serves to introduce the gas.

The theory of the density balance is very simple. The average densities of the two halves of the beam on either side of the central point are very different in virtue of the sealed air bulb on one side. Hence the equilibrium position of the beam depends on the density of the medium in which it is immersed, and for any desired zero position, as read by the microscope, the density of the medium must be the same. If now two sets of measurements are made at the same temperature, one with air in the balance case,

and the other with the experimental gas, then the ratio of the respective pressures, at which the pointer is at the zero position in each case, equals the inverse ratio of the molecular weights of the two gases, or

$$\frac{P_1}{P_2} = \frac{M_2}{M_1}$$

The method has the merits of being very rapid and of requiring only a small quantity of the gas for an accurate determination.

With our instrument, an accuracy of 1 part in 1000 was readily obtainable and, using dry air free from carbon dioxide as a standard of comparison, the molecular weight of the inert gas was found to be 35·1. On the supposition that only argon and helium were present, this corresponded with 13·4 per cent. of the latter in the gas. It followed, therefore, that there were 39 parts of argon, and 6 parts of helium in 100,000 parts by volume of the original spa gas. This quantity is so small that it has no commercial significance.

The nitrogen, oxygen and argon present in the spa gas must be largely derived from the atmosphere and gases which have come into contact with the water on its passage through the soil before being collected again to form the mineral spring. As the spa water is approximately at air temperature on emergence, the relative proportions of the atmospheric gases in the spa gas in equilibrium with the water should be approximately the same as those in which they occur in the atmosphere, provided that disturbing influences have not operated. The ratio of oxygen to nitrogen found in the gas is less than that in the atmosphere, which is to be expected from the chemical reactivity of oxygen. The ratio of argon to nitrogen (1 : 59 by the volume) is, however, greater than that in the atmosphere (1 : 80), but, as the difference is not large, and as the balance may have been disturbed by soil actions in which nitrogen itself plays a part, there is really no evidence that some of the argon has come from a truly subterranean source. The helium, however, is derived without doubt from the presence of minute amounts of radioactive material in the strata through which the spring water has percolated.